



Europäisches Patentamt  
European Patent Office  
Office européen des brevets



Publication number: **0 633 420 A2**

(12)

## EUROPEAN PATENT APPLICATION

(21) Application number: **93830411.0**

(51) Int. Cl.<sup>6</sup>: **F16L 59/06, F17C 3/08,  
H01M 2/10**

(22) Date of filing: **11.10.93**

(30) Priority: **08.07.93 IT MI931481**

(43) Date of publication of application:  
**11.01.95 Bulletin 95/02**

(84) Designated Contracting States:  
**AT DE ES FR GB IT NL SE**

(71) Applicant: **SAES GETTERS S.P.A.**  
**Via Gallarate, 215**  
**I-20151 Milano (IT)**

(72) Inventor: **Boffito, Claudio**  
**Via Papa Giovanni XXIII, 2/14**  
**RHO (Milano) (IT)**  
Inventor: **Conte, Andrea**  
**Piazza Fusina, 1**  
**Milano (IT)**  
Inventor: **Ferrario, Bruno**  
**Via Melzi, 146**  
**Rescaldina (Milano) (IT)**  
Inventor: **Della Porta, Paolo**  
**Strada Priv. delle Acacie, 13**  
**Fagiana-Carimate (Como) (IT)**

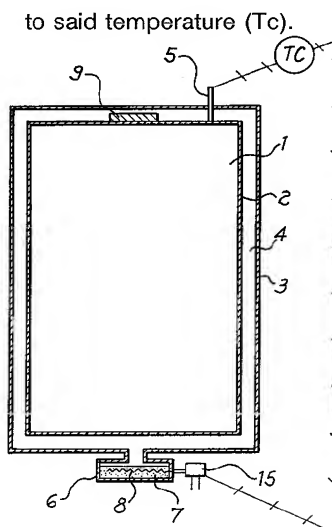
(74) Representative: **Adorno, Silvano et al**  
**c/o SOCIETA' ITALIANA BREVETTI S.p.A.**  
**Via Carducci, 8**  
**I-20123 Milano (IT)**

(54) **Thermally insulating jacket under reversible vacuum.**

(57) A thermally insulating jacket under reversible vacuum, having an inner wall (2), an outer wall (3) and an inner space (4) between said walls in fluid communication with an outer housing (6; 6'; K) containing a reversible non-evaporable hydrogen getter (7; 7') loaded with hydrogen before use, wherein:

a) said reversible hydrogen getter (7; 7') has a hydrogen equilibrium pressure ( $P_{x1}$ ) lower than 100 mbar at 500 °C, when the hydrogen concentration in the getter is 0.1% b.w., and is kept at a variable or constant temperature ( $T_i$ ) essentially different from the temperature ( $T_c$ ) of the hotter wall of the jacket;

b) said inner space (4) contains a non-evaporable promoter getter (9; 9'; 9'') having a hydrogen equilibrium pressure ( $P_{x2}$ ) higher than 100 mbar at 500 °C, when the hydrogen concentration in the getter is 0.1% b.w., which is essentially exposed



**Fig. 2**

**EP 0 633 420 A2**

## BACKGROUND OF THE INVENTION

### 1) Field of the invention

The invention relates to a thermally insulating jacket under reversible vacuum, having a heat-transfer coefficient which changes depending on the different possible situations during the usage, requiring sometimes a fair thermal insulation and sometimes, on the contrary, a rapid heat dissipation.

A jacket of this kind had already been proposed for the insulation e.g. of a heat accumulator; see U.S. Patent 3,823,305. Such a jacket was consisting of an inner wall, an outer wall and an inner space (or inter-space or hollow space) between the two walls; one of the walls of an insulating jacket (in this case the inner one) has obviously to be hotter than the other. Said inner space was typically containing:

(I) a reversible hydrogen getter, namely a getter which can release or reversibly re-adsorb minor or major amounts of hydrogen, depending on the temperature employed for heating or respectively cooling the getter;

(II) a first amount of hydrogen, just chemically adsorbed by said getter in the solid state and depending on the getter temperature;

(III) a second amount of (free) gaseous hydrogen, which takes up the whole available volume inside the jacket; also this second amount depends on the getter temperature.

The hotter the getter the greater the amount of hydrogen shifting from the adsorbed state to the free gaseous state; the colder the getter the lower the amount of free hydrogen, hence its pressure. The higher the hydrogen pressure the higher, within certain limits, the heat-transfer inside the jacket.

A particular field of application of these hydrogen depending jackets are the electrical accumulators installed on the battery-driven cars, even if in a semi-experimental or testing phase. Such batteries, as known, are hot working (300-425 °C) and are generally consisting of a couple lithium/sulphides (425 °C), sodium/sulphur (325 °) or sodium/nickel chloride (300 °C). These batteries must quickly disperse the heat, in case of an overheating, which occurs, depending on the kind of battery, during the discharge phase, as in the case of the sodium/sulphur elements, or during the recharge phase, in the case of the lithium/sulphides batteries.

Apart from these situations, which repeatedly occur, in a cyclical way, during the normal run of a battery, it is also possible to observe emergency situations, as in the case e.g. of a rapid discharge or other, which could lead to a sudden overheating of the elements. In such situations it is equally

important to have an effective means or an effective expedient for rapidly increasing the heat dissipation through the inner space of the jacket.

The overheating can be avoided, as is known, by increasing very quickly the hydrogen pressure in the hollow space of the jacket because of the high thermal conductivity of H<sub>2</sub>. Viceversa, when the conditions engendering the overheating are failing, it is necessary to minimize the heat dispersion in order to avoid a lowering of the temperature of the elements below the optimum efficiency level (300-425 °).

All this can be realized by restoring the low-pressure conditions in the hollow space of the jacket, by letting the reversible getter reabsorb the hydrogen. The thus obtained vacuum, on the other side, tends as is known to worsen with the time and it is therefore unavoidable not only to rapidly create a satisfactory vacuum degree but also to grant the maintenance of said vacuum degree as long as possible.

The double requirement hereinabove (rapid increase and respectively rapid decrease of the hydrogen pressure) can be fulfilled, as a first approximation, by placing a non-evaporable reversible hydrogen getter in an insulated housing outside the jacket and in fluid communication with the same jacket.

An example of such a positioning of the getter according to the known technique is illustrated in Fig. 1. When it is necessary to minimize the insulation, the getter is cooled to room temperature and the hydrogen pressure is consequently lowered, for instance to a level below 1-0.1 Pa in the case of a battery-driven car, whereby the heat dissipation is limited. When it is necessary, on the contrary, to promote the heat dissipation, it is necessary to use an outer or inner electric heating device, which raises the temperature of the getter material; a considerable amount of hydrogen is thus released, which makes the hydrogen pressure rise even up to 1000 Pa, in the case of a battery-driven car.

Again, in this case, of the battery-driven cars, the expression "reversible vacuum" defines the possibility of shifting the vacuum from a minimum value of the working pressure  $\leq 5$  Pa, preferably 1 Pa and even better 0.1 Pa to a maximum operative value  $\geq 50$  Pa and up to 1000 Pa.

### 2) The prior art

A non evaporable reversible hydrogen getter tested in the past was consisting for instance, of only one alloy (Zr-V-Fe) containing (% by atoms) :

Zr: 33% V = 33% Fe = balance.

However, also this reversible alloy doesn't still provide quite satisfactory results as to the manu-

facture, for instance of battery-driven cars; at least the following drawbacks can be in fact registered:

a) the hydrogen release and/or re-adsorption (especially this last passage) are too slow for applications which be at an actually industrial level;

b) said release and/or re-adsorption are even more slow if there is a considerable amount of carbon monoxide or of the other gases, different from hydrogen, usually present in a vacuum chamber ( $\text{CO}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{O}_2$ ,  $\text{N}_2$ ,  $\text{CH}_4$  and so on);

c) the hydrogen release rate and the hydrogen re-adsorption rate, not very high per se since the beginning, decrease rather quickly with the time; it is namely possible to observe a degradation (with the time) of the reversible gettering activity with respect to hydrogen.

Other getters were suggested by U.S. Pat. 4,455,998 but also in this case the results are far from being satisfactory from an industrial point of view.

One object of the instant invention is to grant the creation and the maintenance of a fair vacuum degree in the interspace of the insulating jacket hereinabove.

A second object of the instant invention is to promote the hydrogen release rate and/or the hydrogen re-adsorption rate from and respectively by said reversible hydrogen getter.

A third object of the instant invention is to extend in the time the action of said reversible getters, thus allowing said vacuum degree and said release and re-adsorption rate to long and steadily last at a high level.

A further object of the present invention is to keep said rates at a high level even in the presence of considerable amounts of carbon monoxide and/or other residual gases usually present in a vacuum.

## D I S C L O S U R E

In its broadest aspect, the present invention, allowing to realize the objects hereinabove, resides in a thermally insulating jacket under reversible vacuum, having an inner wall, an outer wall and an interspace between said walls in fluid communication with an outer housing containing a reversible non-evaporable hydrogen getter, loaded with  $\text{H}_2$  before use, wherein:

a) said reversible hydrogen getter has a hydrogen equilibrium pressure lower than 100 mbar (preferably 10 mbar) at  $500^\circ\text{C}$ , when the hydrogen concentration in the getter is 0.1% b.w., and is kept at a variable or constant temperature  $T_i$  essentially different from the temperature  $T_c$  of the hotter wall of the jacket;

b) said inner space contains a non-evaporable promoter getter having a hydrogen equilibrium pressure  $P_{x_2}$  higher than 100 mbar (preferably higher than  $10 P_{x_1}$  and even better  $100 P_{x_1}$ ) at  $500^\circ\text{C}$ , when the hydrogen concentration in the getter is 0.1% b.w., which is essentially exposed to said temperature  $T_c$ .

In a thermally insulating jacket one of the walls is always hotter than the other one, but the hotter wall is not always the inner wall; said promoter getter is preferably in contact just with the hotter wall.

The amount of hydrogen in said reversible hydrogen getter before use is corresponding for instance, in the case of a battery-driven car, to a working pressure, inside the jacket, ranging from 5 Pa (preferably 1 Pa and even better 0.1 Pa), when the temperature is at room level, to 50 Pa (and up to 1000 Pa) when the temperature is at  $500^\circ\text{C}$ .

The Applicant noted, in other words, that the presence of a promoter getter, kept at the temperature  $T_c$  of the hotter wall of the insulating jacket, is extending in the time, in a really surprising and unexpected way, the reversible action of release and respectively re-adsorption of the reversible hydrogen getter. At the same time said promoter getter grants the creation and the long lasting maintenance of an excellent vacuum degree in the interspace of the insulating jackets under reversible vacuum, for instance, in the case of a battery-driven car, between 1 and 0.1 Pa, granting nevertheless the continuity of the action of the reversible hydrogen getter in those emergency cases requiring a massive release of hydrogen.

In the jackets according to the invention the return time, namely the time required by the passage from a pressure of 100 Pa, when said temperature  $T_i$  is  $500^\circ\text{C}$ , to a pressure of 1 Pa, when said temperature  $T_i$  is at room level, can be lower than 10 minutes either in the absence or in the presence of carbon monoxide.

Moreover, the DRT (deep return time), namely the time required by the passage from a pressure of 100 Pa, when said temperature  $T_i$  is  $500^\circ\text{C}$ , to a pressure of 0.1 Pa, when said temperature  $T_i$  is at room level, can be lower than 15 minutes and preferably 12 minutes either in the absence or in the presence of carbon monoxide.

All this did never happen beforehand, notwithstanding the several efforts for selecting an actually effective hydrogen getter for the reversible vacuum. Said return time and DRT are particularly very low when the housing containing the hydrogen reversible getter is provided with heat dispersing blades and fins.

One typical example of said promoter getter is essentially consisting of the Zr-Mn-Fe alloys and more generally of the Zr- $M_2$  alloys, wherein M is a

transition element selected from Cr, Mn, Fe, Co, Ni and mixtures thereof. These alloys are traded by the Applicant as St 909 and are for instance described in U.S. Patent N. 5,180,568 assigned to the Applicant. Other getter alloys suitable for this purpose are the alloys based on titanium and nickel (Ti/Ni), as well as the lanthanum-nickel alloys of the AB<sub>5</sub> type described in EP-A-0,538,622 and the HM and LM alloys (Ti-V alloys containing a high or respectively low amount of manganese) mentioned in the Italian patent application MI 93 A 000851 in the name of the Applicant.

One typical example of said non-evaporable reversible hydrogen getters is consisting of zirconium and/or titanium, of the Zr-Al alloys (see U.S. Patent N. 3,780,501) and of the alloys containing zirconium and vanadium, in particular the Zr-V-Fe alloys, described for instance in U.S. Patent N. 4,312,669 and 4,839,085; really excellent results were obtained from the alloys traded by the Applicant as St 707, having following composition (by weight):

Zr = 70% V = 24,6% Fe = balance.

More generally, said reversible hydrogen getter may be a non-evaporable ternary alloy Zr-V-Fe having a percent composition (by weight) which, when recorded on a diagram suitable for ternary compositions, is lying inside a polygon having at its vertices the points defined as follows:

- a) 78% Zr - 20% V - 2% Fe
- b) 45% Zr - 20% V - 35% Fe
- c) 48% Zr - 50% V - 2% Fe

Still more preferably said reversible hydrogen getter may be a non-evaporable ternary alloy Zr-V-Fe having a percent composition (by weight) which, when recorded on a diagram suitable for ternary compositions, is lying inside a polygon having at its vertices the points defined as follows:

- d) 70% Zr - 35% V - 5% Fe
- e) 70% Zr - 24% V - 6% Fe
- f) 66% Zr - 24% V - 10% Fe
- g) 47% Zr - 43% V - 10% Fe
- h) 47% Zr - 45% V - 8% Fe
- i) 50% Zr - 45% V - 5% Fe.

It is finally possible to use mixtures of said reversible hydrogen getters and mixtures of said promoter getters, each for the respective functions.

The two kinds of getter (reversible and promoter) are installed separately. The Applicant noted however that whenever the reversible hydrogen getter is coated with a thin protective layer of promoter getter, essentially kept at the same temperature T<sub>i</sub> of the reversible hydrogen getter, the constancy of the high release and re-adsorption rates of the reversible hydrogen getter is even more prolonged. The protective layer of promoter getter, in its turn, may be advantageously surmounted by a porous septum made from metal,

ceramics, glass or other equivalent material. Said protective layer may be also consisting of a second promoter getter different from the separate promoter getter kept at a constant T<sub>c</sub> temperature instead of T<sub>i</sub>

Generally the ratio between the mass of said protective layer and the sum of the mass of said reversible hydrogen getter and of the mass of the promoter getter exposed to said temperature T<sub>c</sub> is from 0.001 : 1 to 1:1 and preferably from 0.01 : 1 to 0.5 : 1.

The reversible hydrogen getter is loaded, before use, with a calibrated amount of hydrogen allowing to reach, in the hot phase, the predetermined pressure in the interspace of the insulating jacket, naturally when it is required to change the vacuum conditions.

Either the reversible hydrogen getter or the promoter getter may be used in the form of a powder, optionally placed in a housing having at least one porous wall. Said powder has generally an average particle size from 0.1 to 500 micrometer, preferably from 0.1 to 250 micrometer and even better from 0.1 to 125 micrometer. Very satisfactory results can be obtained if at least 85% by volume of the particles has an average size lower than 100 micrometer and where in the volume percentage of the particles having an average size lower than 15 micrometer is equal to or lower than 10%.

Said powder, however, may be converted, before use, into shaped bodies like pellets, granules, tablets, rings, saddles, coated strips and similar.

The shaping of said bodies may be carried out by means of compression and sintering; in its turn said sintering may be carried out by means of a simple heating or resorting both to a heating and to the presence of a second powder, as is described for instance in GB-A-2,077,487, thus reaching a rather high porosity degree. The average size of said shaped bodies is a few millimeter, generally from 0.5 to 5 mm.

Good results are obtained when the separate promoter getter (temperature = T<sub>c</sub>) is in contact with the hotter wall, in the form of a toroidal belt or strip or of a simple layer or thin plate lying on a plane surface of a jacket's wall.

The interspace of said jacket may be empty or alternatively filled, in a partial or complete way by a solid insulating material like for instance an expanded polymer (polystyrene, phenol-formaldehyde resins, polyacetalic resins and so on) having a very low density.

The shape of the jackets according to the invention may be e.g.:

- the cylindrical shape;
- the hemicylindrical shape;

- the shape of two hemicylinders, wherein the first is under reversible vacuum and the second is under stable vacuum or under reversible vacuum.

The reversible insulating jacket according to the present invention may be applied with considerable advantage to many different kinds of apparatuses; we quote, for merely exemplificative purposes, the heat accumulators, the solar panels, the electric accumulators and the cryogenic vessels (Dewar) having a wide size, especially if they have to be rapidly loaded and unloaded, with a high temperature gradient. We quote as well the catalytic silencers of cars and trucks, which could be insulated in a variable way, depending on the operative conditions.

A few aspects of the present invention will be evident to a skilled in the art by referring to the following description and examples, which are however supplied for merely illustrative and non limitative purposes, while referring to the attached drawings wherein:

FIGURE 1 is the cross-section of an insulating jacket under reversible vacuum according to the prior art;

FIGURE 2 is a similar cross-section of an insulating jacket under reversible vacuum according to the present invention;

FIGURE 3 is a variant of figure 2, wherein the promoter getter surrounds as a toroidal strip the inner cylindrical wall and is in contact with the same inner wall;

FIGURE 4 illustrates a different way of housing the reversible hydrogen getter, with respect to figures 2 and 3, wherein, according to a variant represented in FIGURE 4a, the gettering mass is completely contained in a porous septum (diaphragm, filter) in the form of an enveloping foil;

FIGURE 5 is a cross-section of a device of the type indicated in figure 4, containing the reversible hydrogen getter coated by a protective layer of promoter getter and surmounted by a porous septum;

FIGURE 6 is a cross-section a long line VI-VI of figure 5;

FIGURE 7 is a partial view of a cross-section of a housing loaded with reversible hydrogen getter and provided with heat dispersing fins;

FIGURE 8 schematically represents the facilities realized by the Applicant on a laboratory scale, in order to carry out the examples of the instant patent application;

FIGURES 9 and 10 schematically show the cross-section of the housings containing respectively the reversible hydrogen getter and the promoter getter, as used in the examples;

FIGURES 11 and 12 report as a plot the results of the examples;

FIGURE 13 is an example of insulating jacket having a particular (hemicylindrical) shape, suitable for catalytical silencers.

Referring now to figures 2 and 3 a space which has to be thermoregulated, for instance a battery working in the hot to be installed on a battery-driven car, is surrounded by an inner cylindrical wall 2 forming, together with the outer cylindrical wall 3, an insulating jacket, wherein a predetermined degree of vacuum does exist in the interspace 4 of said jacket. A thermocouple 5 is connected, by means of a temperature controller TC, to a small housing 6, outside the insulating jacket, which is kept at a temperature different from the jacket's temperature. In said housing 6, in fluid communication with the interspace 4, there is a reversible hydrogen getter 7, for instance a Zr-V-Fe alloy, in the form of a powder or of pellets, tablets or others, which can be quickly heated or cooled by a thermal element 8, connected to a thermostat 15, operated in its turn by the temperature controller TC.

Referring again to figures 2 and 3, the interspace 4 contains also a separate promoter getter 9 or 9', exposed to a temperature  $T_c$ , which succeeds in accelerating and stabilizing in the time, in a really surprising way, either the  $H_2$  emission rate (or release rate) or the  $H_2$  re-adsorption rate of the reversible hydrogen getter 7.

With reference to figure 4, a reversible hydrogen getter 7' is lodged in a cylindrical housing 6' provided with an electric heating element 8', coaxial with said housing 6'. Said heating element 8' may be directly immersed in the getter material or may be arranged outside in a recess of the wall of the housing 6'.

Figure 5 shows an improvement consisting of a coating of the reversible hydrogen getter 7' with a thin protective layer of promoter getter 10, surmounted by a porous diaphragm 11, which remarkably prolongs, at a high level, the high  $H_2$  emission rate and  $H_2$  re-adsorption rate of the reversible hydrogen getter.

Figure 6 is cross-section a long line VI-VI of figure 5, showing the possibility of inserting into the getter mass a crown of blades 12, plane or curved, made from a heat conducting material in order to improve the heat-transfer either during the heating of the reversible hydrogen getter or-especially-during its cooling. Figure 7 in its turn is the partial cross-section of a housing, here still provided with blades as in figure 6, having outer walls supplied with fins (13) even more promoting the thermal dispersion. Naturally, the housing of figure 7 could be of whatsoever other type and not necessarily provided with blades.

Figures from 8 to 12 are described in detail in the examples hereinbelow.

Figure 13 shows an insulating jacket under reversible vacuum having a hemicylindrical shape, provided with inner promoter getter 9" and outer housing 6" containing the reversible hydrogen getter, optionally coated with a thin layer of promoter getter.

As an alternative, one may use two hemicylindrical jackets, both under reversible vacuum or the first under stable vacuum (16) and the second under reversible vacuum, the one near the other as to simulate a cylindrical jacket. The nozzle putting in fluid communication the jacket and the housing 6" may be in the position indicated in figure 13 or in whatsoever other suitable position.

The following examples are supplied for merely illustrative purposes and do not limit in any case the scope and the spirit of the invention. The experimental work was carried out using an empty interspace, but is possible to obtain great advantages also with an interspace partially or completely filled with solid insulating material.

#### EXAMPLE 1

The facilities traced in figure 8 are consisting of two volumes V1 and V2 of respectively 0,5 and 2 liter, connected each other by means of a valve v1. Volume V1 is in communication, by means of valve v4, with a pumping system for ultra-high vacuum (UHV), consisting of a turbomolecular pump X and of a rotary pump Y provided with blades. In the volume V1 there are introduced known amounts of hydrogen and carbon monoxide, coming from two flasks by means of metering valves v2 and v3. The gas pressure in the volume is recorded by two capacitive manometers C1 and C2 having respectively a maximum recordable pressure of 133,000 Pa and 100 Pa, in order to cover a wider pressure range. A recent example of capacitive manometers is described in the international patent application WO 93/11415. The volume V2 contains two devices (DCR), respectively illustrated in detail in figure 9 and figure 10, for the housing and the heating of the gettering metal powders.

They are essentially consisting of a cylindrical coil resistance R, surrounding a cylindrical housing K, made from hardened steel, filled with getter material. The first DCR device (A+B), represented in figure 9, contains 500 mg of a reversible hydrogen getter consisting of a Zr-V-Fe alloy (70% b.w. Zr; 24,6% b.w. V; balance Fe) traded by the Applicant as St 707.

The equilibrium pressure  $Px_1$  of such alloy, at 500°C and for a  $H_2$  concentration in the alloy equal to 0,1% b.w., is approximately 0.05 torr (6.67 Pa or 0.0667 mbar). Said alloy is surmounted by a protective layer (300 mg) of promoter getter con-

sisting of a Zr-Mn-Fe alloy (45.4% Zr; 27.3% Mn; balance Fe) traded by the Applicant as St 909.

Such second alloy, corresponding to the inter-metallic compound Zr-Mn-Fe, of the  $AB_2$  type, shows a hydrogen equilibrium pressure  $Px_2$ , at 500°C and for a  $H_2$  concentration in the alloy equal to 0.1% b.w., higher than 1 bar (100,000 Pa), as per the article of D. Shaltiel et al. [J. of the Less Common Metals, 53 (1977) 117-131; see in particular Table 3 at page 125]. The second DCR device (C), represented in figure 10, contains 500 mg of said promoter getter (St 909. In both the housings the getters are surmounted by a high porosity filter retaining the powder. Granulometry:

- for the St 707 alloy: from 0.1 to 125  $\mu m$ ;
- for the St 909 alloy: from 0.1 to 125  $\mu m$ .

At the outset, the two materials underwent an activation treatment and the pumping system allowed to reach a residual pressure lower than  $10^{-4}$  Pa. By supplying then a suitable input voltage to the resistance of the DCR devices, the getter powders were heated until reaching the temperature of 600°C - The two DCR devices were kept at such temperature for 1 h keeping the vacuum pumps continuously running.

Once the activation was over, the DCR device (A+B) was brought back to room temperature; the DCR device (C), on the contrary, was stabilized at 350°C by means of the temperature controller (TC2). The system was then isolated from the vacuum pumps by closing valve v4 and successively, while closing valve v1 and suitably regulating the metering valve v2, there was introduced into volume V1 (0,5 liter capacity) an amount of hydrogen sufficient for reaching a pressure of 8000 Pa. By opening valve v1, the hydrogen was made to expand into volume V2, where it was adsorbed by the DCR devices. When the hydrogen was practically adsorbed in a complete way (residual pressure in the vacuum chamber lower than 0.01 Pa) the DCR device (A+B) was alternatively brought in a cyclical way, from room temperature to 500°C and then again to room temperature and so on, by means of a temperature controller and of a programmed timer. The temperature  $T_c$  of the DCR device (C) was kept at a constant level (350°C). Contemporaneously it was recorded the continuous change of the hydrogen pressure in the system, a long with the temperature of the two DCR devices. It was noted that when the DCR device (A+B) was at room temperature since a long time the hydrogen pressure fell below 0.1; when the temperature was then raised to 500°C and brought back to room level the time required by a reduction of the pressure below 1 Pa was lower than 10 minutes (return time) and the time required by a reduction of the pressure below 0.1 Pa (DRT namely Deep Return Time) was lower

than 15 minutes (12 minutes in the case of a Zr V<sub>2</sub> alloy as the reversible H<sub>2</sub> getter). On occasion of the raising of the temperature to 500 °C the time was much shorter, approximately 3 minutes.

Irregularly, during the heating-cooling cycles, there were gradually introduced into the system increasing amounts of carbon monoxide (CO) until reaching an overall amount of 1.3 Pa. m<sup>3</sup>.

This had no appreciable influence on the pressure values at 500 °C either on the time required for reaching such values; only when the single dosed quantities of carbon monoxide were higher than 0.6 Pa. m<sup>3</sup> it was registered a small slowing of the pressure decrease in the cooling phase but only for the first two or three cycles. Successively, after the first three cycles, the pressure course began again to be favourable.

The trend of the cycles is indicatively recorded on figure 11.

#### EXAMPLE 2 (COMPARATIVE)

Example 1 was repeated by replacing the St 909 alloy of both the protective layer (temperature = T<sub>i</sub>) and the separate promoter getter (temperature = T<sub>c</sub>) by equal amounts of zirconium hydride, having a H<sub>2</sub> equilibrium pressure lower than the H<sub>2</sub> equilibrium pressure P<sub>x1</sub> of the reversible hydrogen getter (St 707 alloy). The results, either in the presence of hydrogen alone or after the addition of carbon monoxide (CO) were clearly worse with respect to example 1.

The pressure did never fall in fact below 1 Pa even after 40 minutes. The trend of the comparative cycles is indicatively recorded on figure 12 (concerning only the cooling phase from 500 °C to 25 °C).

#### Claims

1. A thermally insulating jacket under reversible vacuum, having an inner wall (2), an outer wall (3) and an inner space (4) between said walls in fluid communication with an outer housing (6; 6'; K) containing a reversible non-evaporable hydrogen getter (7; 7') loaded with hydrogen before use, wherein:
  - a) said reversible hydrogen getter (7; 7') has a hydrogen equilibrium pressure (P<sub>x1</sub>) lower than 100 mbar at 500 °C, when the hydrogen concentration in the getter is 0.1% b.w., and is kept at a variable or constant temperature (T<sub>i</sub>) essentially different from the temperature (T<sub>c</sub>) of the hotter wall of the jacket;
  - b) said inner space (4) contains a non-evaporable promoter getter (9; 9' ; 9'') having a hydrogen equilibrium pressure (P<sub>x2</sub>)

higher than 100 mbar at 500 °C, when the hydrogen concentration in the getter is 0.1% b.w., which is essentially exposed to said temperature (T<sub>c</sub>).

2. An insulating jacket according to claim 1, wherein the amount of hydrogen in said reversible hydrogen getter (7; 7') before use is corresponding to a working pressure inside the jacket, ranging from 5 Pa (preferably 1 Pa and even better 0.1 Pa), when the temperature is at room level, to 50 Pa (or up to 1000 Pa) when the temperature is at 500 °C.
3. An insulating jacket according to claim 1, wherein said promoter getter (9; 9'; 9'') is essentially in contact with said hotter wall.
4. A jacket according to claim 1, wherein said pressure (P<sub>x1</sub>) is lower than 10 mbar and wherein said pressure (P<sub>x2</sub>) is higher than 10 P<sub>x1</sub> and preferably 100 P<sub>x1</sub>.
5. A jacket according to claim 1, wherein said reversible hydrogen getter (7') is coated with a protective layer (10) of said promoter getter, which is essentially kept at the same temperature (T<sub>i</sub>) of said reversible hydrogen getter (7').
6. A jacket according to claim 5, wherein said protective layer (10) is surmounted by a porous septum (11).
7. A jacket according to claim 1, having a characteristic working pressure ranging from 1 Pa (preferably 0.1 Pa), when the temperature is at room level, to 100 Pa, when the temperature is 500 °C.
8. A jacket according to claim 1, having a characteristic return time, namely the time required by the passage from a pressure of 100 Pa, when said temperature (T<sub>i</sub>) is 500 °C, to a pressure of 1 Pa, when said temperature (T<sub>i</sub>) is at room level, lower than 10 minutes either in the absence or in the presence of carbon monoxide.
9. A jacket according to claim 1, having a characteristic DRT (deep return time), namely the time required by the passage from a pressure of 100 Pa, when said temperature (T<sub>i</sub>) is 500 °C, to a pressure of 0.1 Pa, when said temperature (T<sub>i</sub>) is at room level, lower than 15 minutes, and preferably 12 minutes, either in the absence or in the presence of carbon monoxide.

10. A jacket according to claim 1, wherein said promoter getter is selected from the alloys Zr M<sub>2</sub>, wherein M is a transition element selected from Cr, Mn, Fe, Co, Ni and mixtures thereof.
11. A jacket according to claim 1, wherein said promoter getter is selected from:
- i) the zirconium-manganese-iron alloys (Zr, Mn, Fe);
  - ii) the HM alloys, namely the titanium-vanadium alloys having a high manganese content;
  - iii) the LM alloys, namely the titanium-vanadium alloys having a low manganese content;
  - iv) the titanium-nickel alloys and/or the lanthanum-nickel alloys of the AB<sub>5</sub> type;
  - v) mixtures thereof.
12. A jacket according to claim 1, wherein said reversible hydrogen getter is selected from:
- i) the alloys containing zirconium and vanadium and in particular the zirconium-vanadium-iron alloys;
  - ii) the zirconium-aluminum alloys;
  - iii) zirconium and/or titanium;
  - iv) mixtures thereof.
13. A jacket according to claim 12, wherein said reversible hydrogen getter is a non-evaporable ternary getter alloy having a percent composition (by weight) which, when recorded on a diagram suitable for ternary compositions, is lying inside a polygon having at its vertices the points defined as follows:
- A) 78% Zr - 20% V - 2% Fe
  - B) 45% Zr - 20% V - 35% Fe
  - C) 48% Zr - 50% V - 2% Fe.
14. A jacket according to claim 1, supplied with a heating device (R) which is outside said housing (K) containing said reversible hydrogen getter.
15. A jacket according to claim 1, supplied with a heating device (8') which is directly immersed in said reversible hydrogen getter.
16. A jacket according to claim 15, wherein said heating device (8') is supplied with heat dispersing blades (12).
17. A jacket according to claim 1, wherein said housing (6') is supplied with heat dispersing fins (13).
18. A jacket according to claim 1, wherein said inner space (4) is partially or completely filled with solid insulating material, in particular polystyrene, phenolformaldehyde resins, polyacetalic resins and combinations thereof.
19. A jacket according to claim 6, wherein the ratio between the mass of said protective layer (10) and the sum of the mass of said reversible hydrogen getter (7') and of the mass of the promoter getter exposed to said temperature (T<sub>c</sub>) is from 0.001:1 to 1:1 and preferably from 0.01:1 to 0.5:1.
20. A jacket according to claim 1, wherein said reversible hydrogen getter and/or said promoter getter are in the form of shaped bodies like pellets, granules, tablets, rings, saddles, coated strips and similar.
21. A jacket according to claim 1, wherein said reversible hydrogen getter and/or said promoter getter are in the form of a powder.
22. A jacket according to claim 21, wherein at least 85% by volume of the particles has an average size lower than 100 micrometer and wherein the volume percentage of the particles having an average size lower than 15 micrometer is equal to or lower than 10%.
23. A jacket according to claim 1, having a shape selected from:
- the cylindrical shape;
  - the hemicylindrical shape;
  - the shape of two hemicylinders, wherein the first is under reversible vacuum and the second (16) is under stable vacuum or under reversible vacuum.
24. A thermally insulated apparatus selected from:
- heat accumulators;
  - electrical accumulators and in particular batteries for accumulator traction;
  - cryogenic vessels (DEWAR) and cryogenic pipes;
  - catalytic silencers for motor vehicles;
  - solar panels;
- supplied with the thermally insulating jacket according to claim 1.



Fig. 1

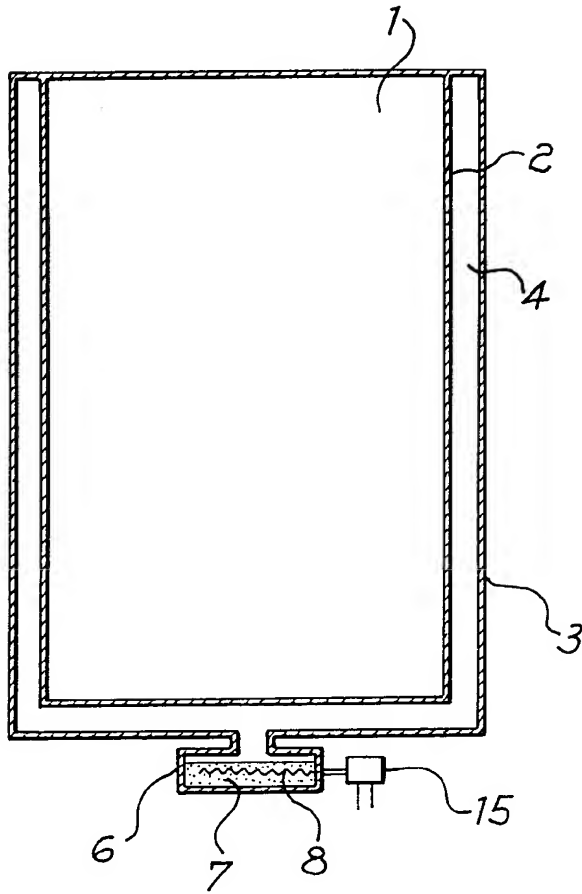


Fig. 7

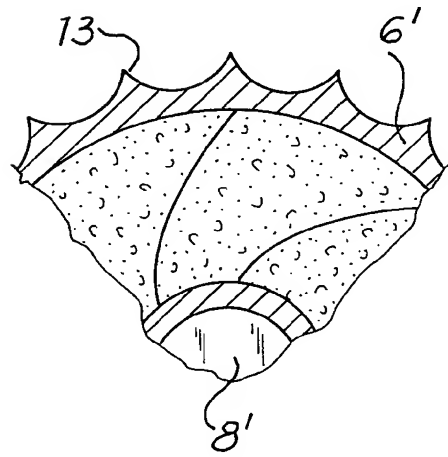
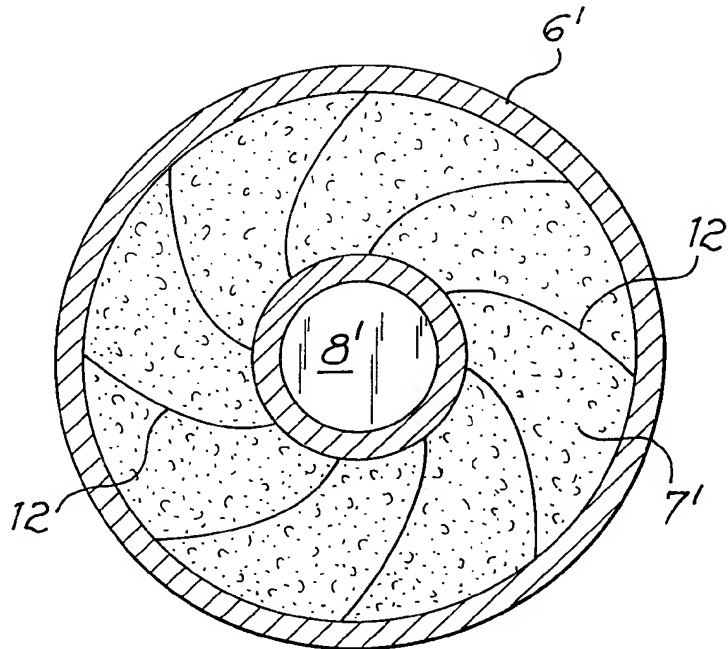


Fig. 6



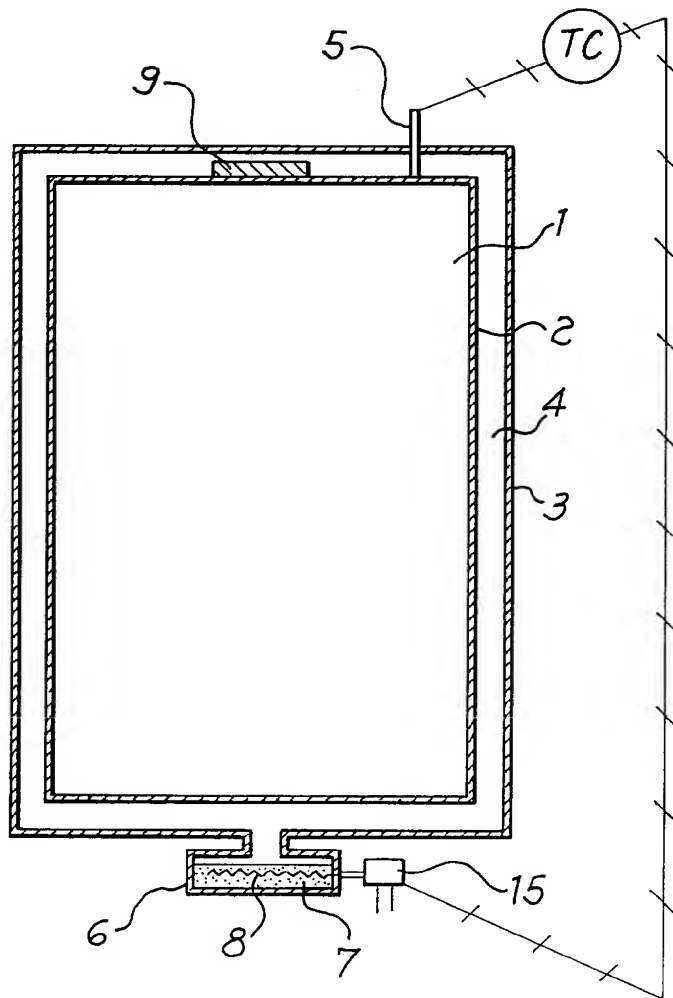


Fig. 2

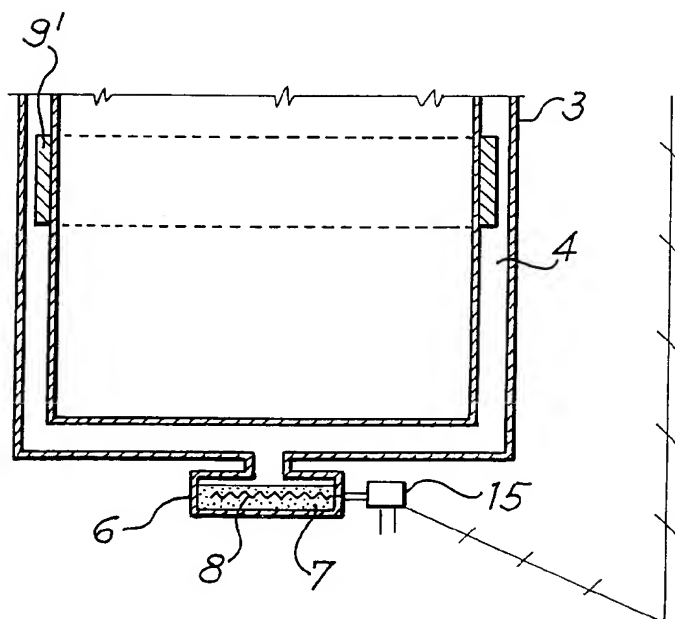
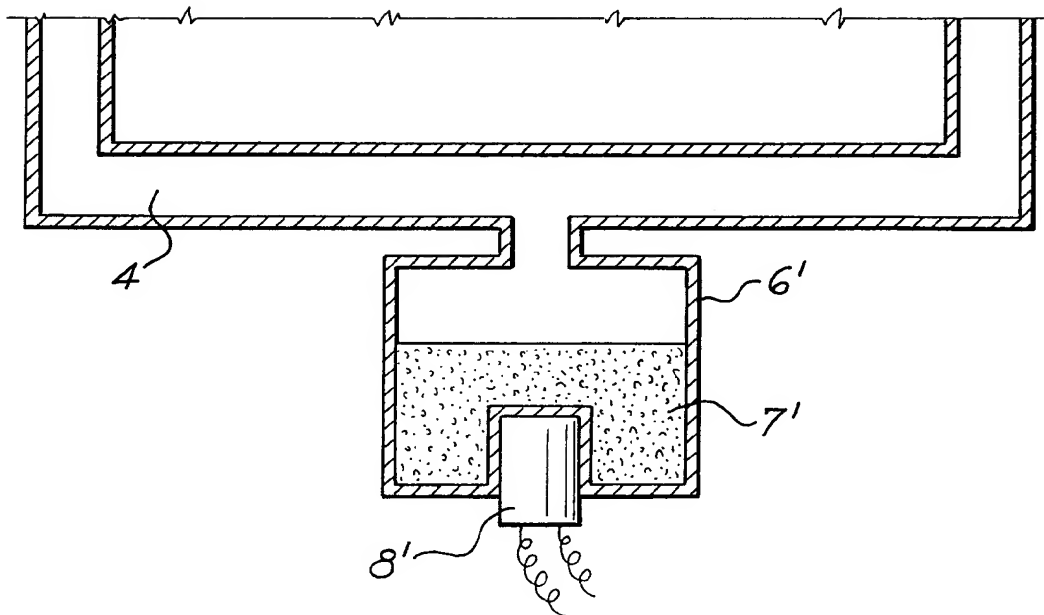


Fig. 3

*Fig. 4*



*Fig. 5*

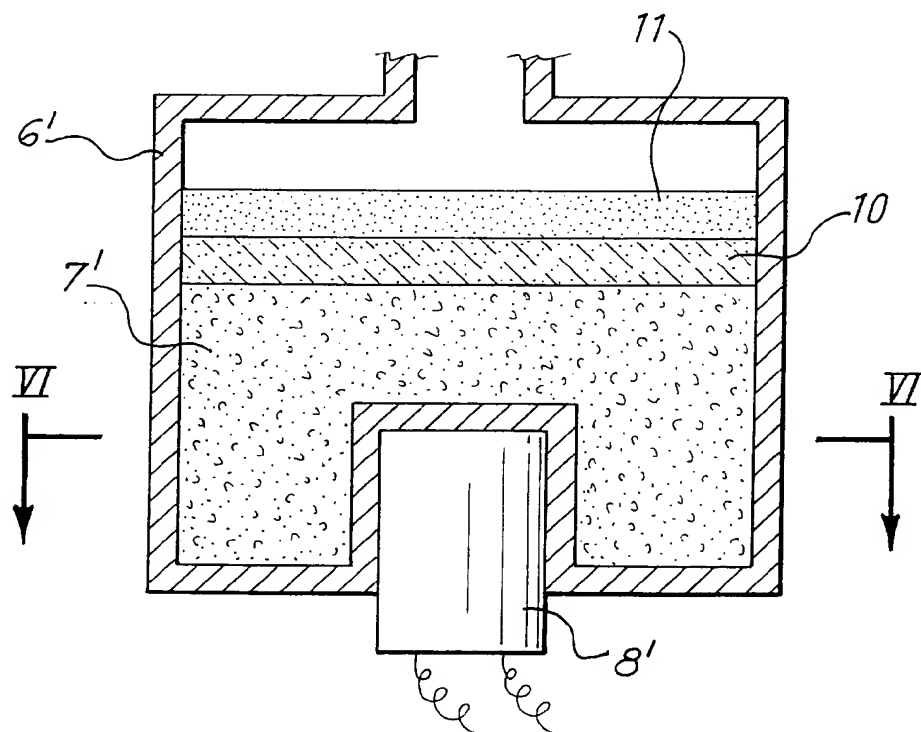


Fig. 8

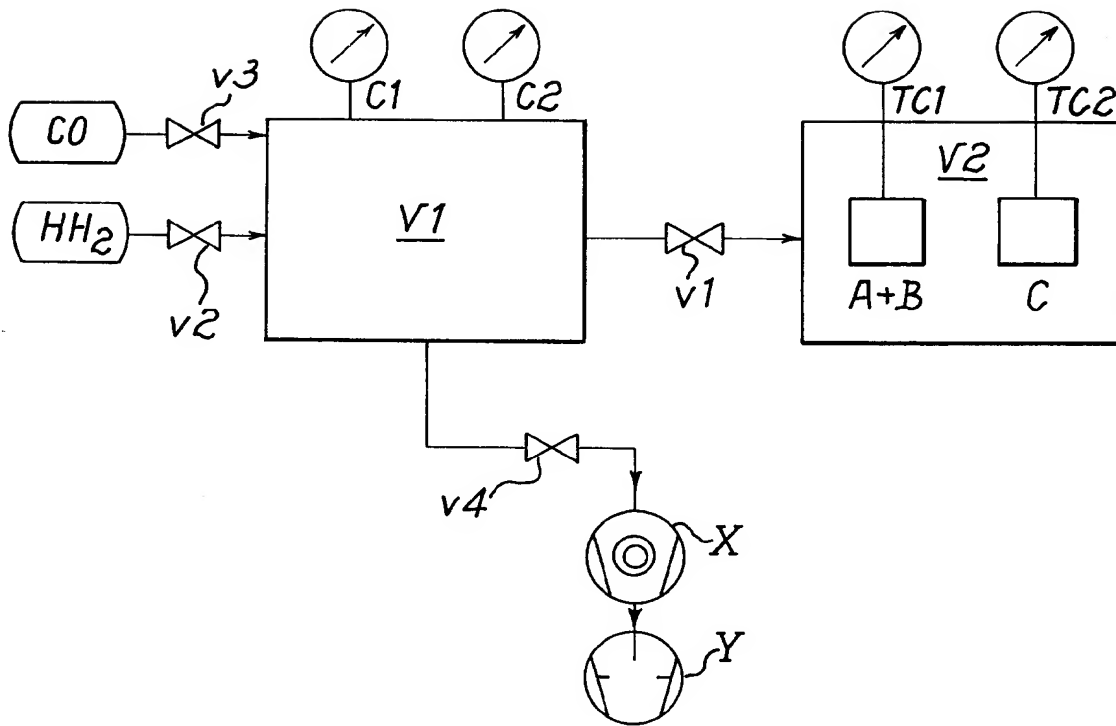


Fig. 9

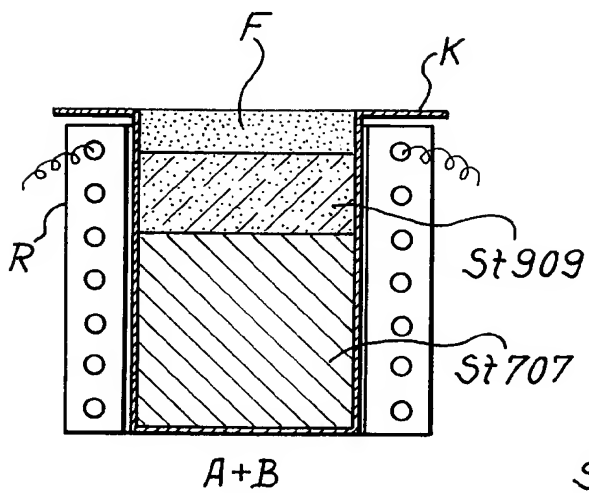
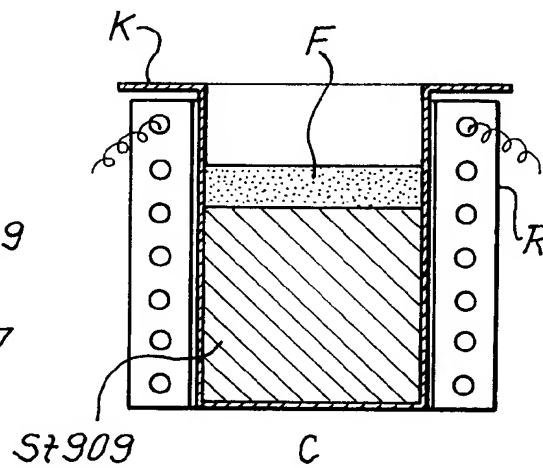
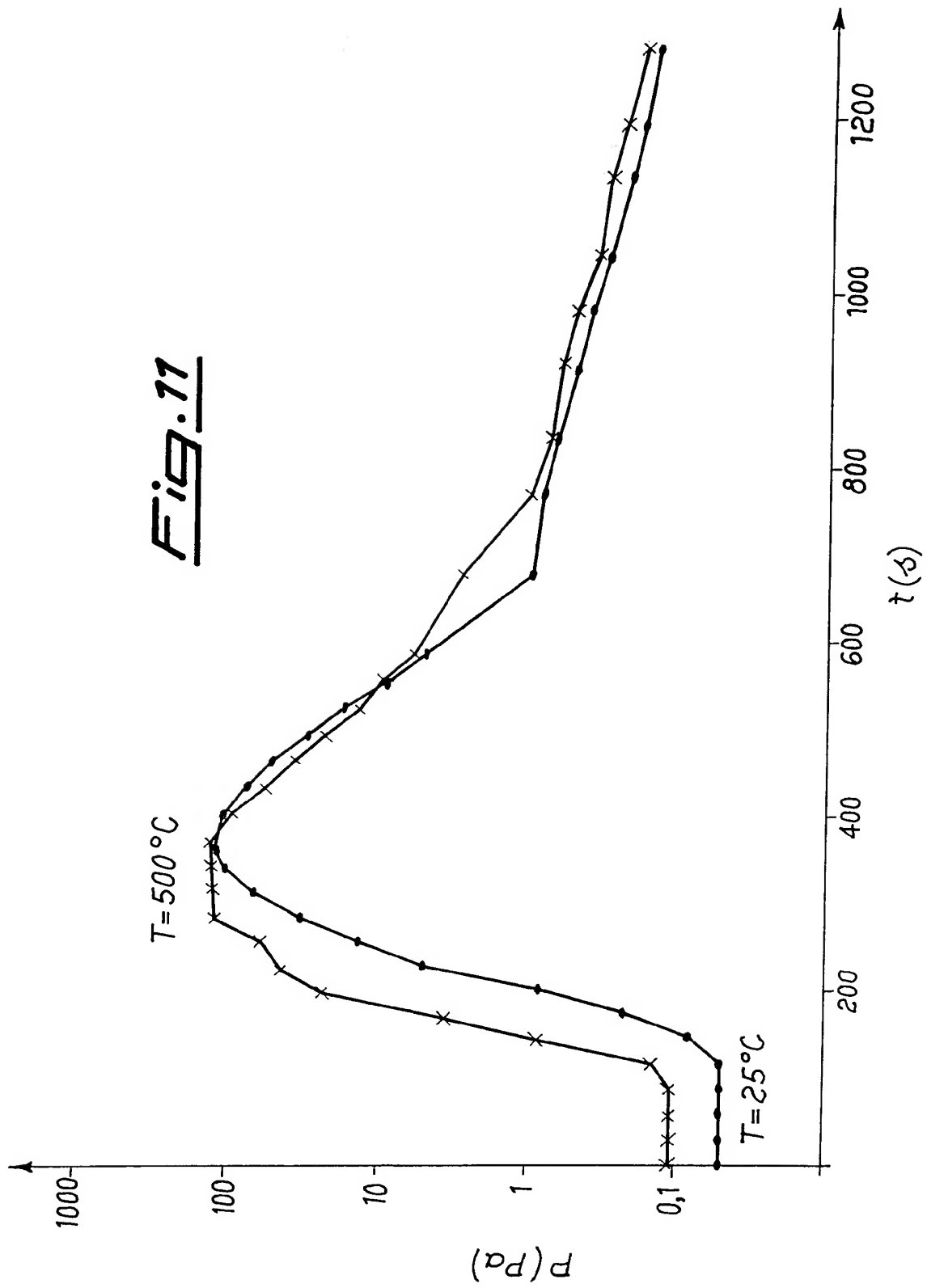


Fig. 10





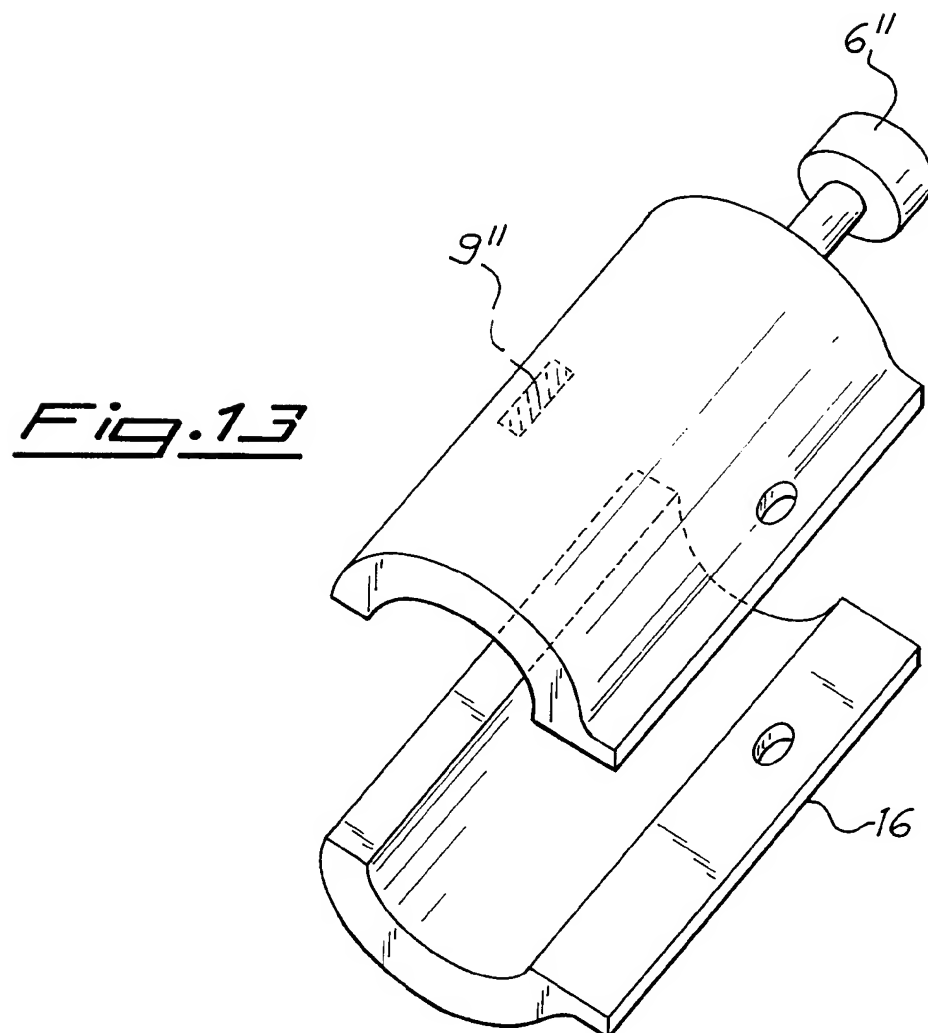
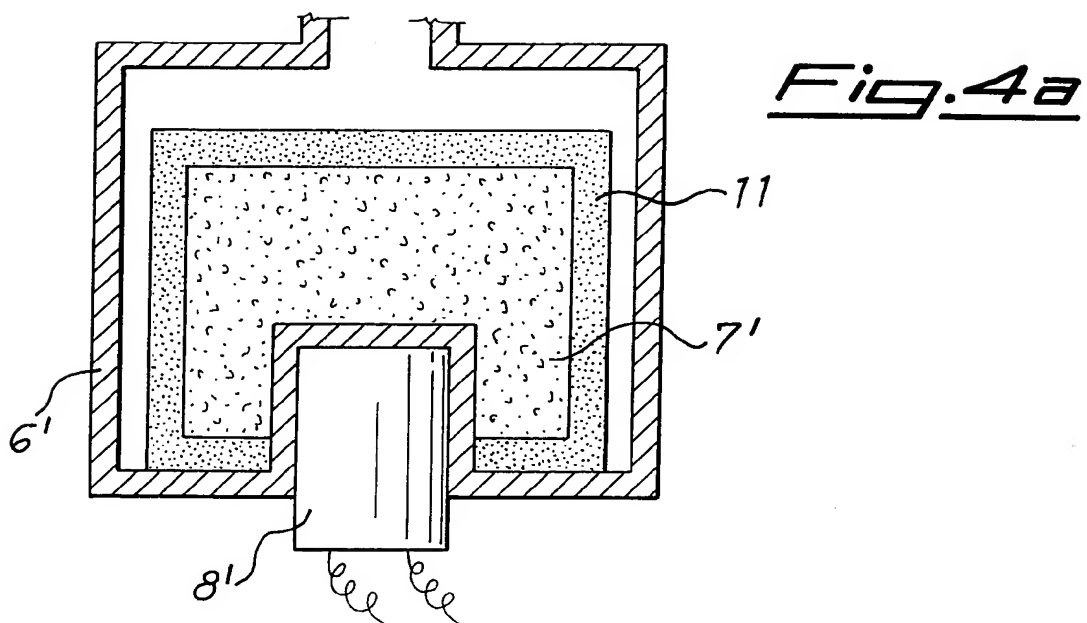


Fig. 12